

## FT-IR QUANTIFICATION OF INDUSTRIAL HYDRAULIC FLUIDS IN PERCHLOROETHYLENE

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## ABSTRACT

Freon-113 is the primary test solvent used for validating cleaned aerospace hardware at NASA Kennedy Space Center. In 1995, due to the ozone depletion problem, the United States policy called for complete phase out of Freons. This work was carried out to investigate whether perchloroethylene can be used as an alternate clean validation and extraction solvent for the quantitative analysis of industrial hydraulic fluids residue as non-volatile residue material by infrared spectroscopy. The results indicate that monitoring peak areas in the ester infrared spectral ( $\sim 1753\sim 1708$ )  $\text{cm}^{-1}$  region with a mercury-cadmium-telluride detector, it is possible to detect  $\sim 1$  mg/L of hydraulic fluids in perchloroethylene

## INTRODUCTION

**Objective:** To investigate whether perchloroethylene (PCE) can be used as an extraction solvent for the detection of industrial hydraulic fluids residue on small aerospace hardware as non-volatile residue (NVR) material at low ( $\sim 1$  mg/L) concentration levels by infrared spectroscopy for meeting the strict NASA Kennedy Space Center (KSC) specifications of  $\sim 2$  mg/ft<sup>2</sup> for the NVR material in precision cleaning verification.

**Background:** 1,1,2 trichloro-1,2,2 trifluoro ethane (CFC-113) known as Freon-113 is a primary test solvent used for validating cleaned aerospace hardware at KSC. For a safe space shuttle launch, it is of utmost importance that the hardware be verified clean of organic materials before use in an oxygen rich environment as that of the Orbiter. KSC standard validating procedure calls for the extraction of organic materials with Freon-113, and subsequent determination of NVR material by gravimetric method<sup>1</sup>.

Freons are known to remain in the atmosphere long enough to migrate to altitudes due to their high volatility, and are proven threat to the earth's protective ozone layer. The present United States Government policy calls for complete ban on the industrial production and use of these compounds.

A 1993 preliminary report<sup>2</sup> by the U. S. Environmental Protection Agency (USEPA) on the efforts to replace Freon-113 for the determination of oils and greases suggested the evaluation of infrared-based methods, and PCE as an alternate NVR extraction solvent. In the summer of 1993, the chlorofluorocarbon replacement group at KSC decided to pursue the recommendations of the USEPA preliminary report since PCE has high solvation compatibility with organics, generally considered non-toxic (OSHA LD<sub>50</sub>), and has a high B.P. (121 °C) compared to 48 °C for Freon-113. The results indicated<sup>3</sup> the feasibility of detecting  $\sim 20$  mg/L of industrial hydraulic fluids in PCE by monitoring the absorbance intensity of the ester infrared spectral peak ( $\sim 1738$   $\text{cm}^{-1}$ ) with a DTGS detector. The findings were encouraging to extend the infrared method to low mg/L level detection work utilizing a more sensitive liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector<sup>4</sup>.

The results presented are the outcome of the efforts on the detection of low concentration levels (1-20 mg/L) of industrial hydraulic fluids residue on small aerospace hardware as NVR material by infrared spectroscopy utilizing ester spectral peak (absorption) region. The report reflects the possibilities of utilizing infrared method for the quantification of hydraulic fluids in PCE as well as replacing Freon-113 with PCE for extracting NVR material from small aerospace hardware for precision cleaning verification.

## MATERIALS AND METHODS

The spectrometer used for this study was a Mattson Galaxy series 3000 FT-IR spectrometer having a liquid nitrogen cooled MCT detector, and was operated from a computer-based data-collection and spectral analysis analytical package called FIRST. The spectra were obtained using the setting of

120 interferogram scans at  $4\text{ cm}^{-1}$  resolution. Zinc selenide (ZnSe) variable path length liquid infrared cell was used for recording the spectra since it has high resistance to humidity and organic solvents, and has low absorption in Infrared range.

Three of the ester-based hydrocarbon type hydraulic fluids most commonly used at KSC were used for the development of calibration curves. They were Red MIL-H-5606, Yellow Tapmatic Cutting Fluid and Red MIL-H-83282, and were supplied by the Materials Science Branch at KSC. Perchloroethylene used was a Fisher Brand Reagent Grade solvent having 0.5% of ethyl alcohol as stabilizer.

Small aerospace hardware in quantities are used at KSC. Parts (cleaned as well as tainted with hydraulic fluids) which could fit into the mouth of 2 oz. amber bottles were used for analyte spiking and PCE extraction work. They were obtained from the machine shop of the Material Science Branch at KSC.

#### **Test Procedure:**

**Small Parts (Verified Clean) Cleaning Procedure:** Parts were placed in a small plastic tray containing water and laboratory detergent. The tray was placed in an ultrasonic bath for few minutes. The parts were rinsed thrice with deionized water before placing them again in the ultrasonic bath with acetone for a few minutes. The samples were dried at room temperature, and preserved in plastic zip-lock bags before analysis.

**Gravimetric Method for the Determination of NVR:** 25 ml of an aliquot was transferred in a pre-cleaned and pre-weighed 30 ml beaker. The covered beaker containing the sample was placed overnight in a laboratory oven maintained at  $90^{\circ}\text{C}$ . After complete evaporation of the solvent, the beaker was placed in a dessicator for 30 minutes before exposing the beaker to room temperature and humidity conditions for 15 minutes for final weighing. A solvent blank was always run with a set of samples.

**NVR Extraction Procedure with PCE:** 50 ml of PCE was placed in a 2 oz amber bottle. Pre-selected small parts of different sizes were placed in the bottle until the level of the solvent was below the neck of the bottle. After capping, the contents of the bottle was given various gentle swirl motions for extracting NVR material from the parts.

## **RESULTS AND DISCUSSIONS**

ASTM D 3921-85 "Standard Method<sup>5</sup> for Oil and Grease and Petroleum Hydrocarbons in Water" utilizes absorbance of the infrared band of the  $\text{CH}_2$  group at  $\sim 2930\text{ cm}^{-1}$  (asymmetric stretch) for calibration purposes. Efforts to utilize absorbance data of  $\text{CH}_2$  band proved fruitless for the preparation of calibration curve since spectra recorded for hydraulic fluids at low concentration levels in PCE demonstrated a lot of spectral activity in this generic  $\text{CH}_2$  stretching band area under the experimental conditions.

Ester  $\text{C}=\text{O}$  group when conjugated with  $\text{C}=\text{C}$  groups or aromatic rings absorb<sup>6</sup> at ( $\sim 1740\sim 1715$ )  $\text{cm}^{-1}$ , and was studied for the development of calibration curves for the detection of PCE extractable hydraulic fluids residue as NVR material on small aerospace hardware. Erratic net ester spectral peak intensity data was obtained for series of standard dilutions in the range of 1-20 mg/L concentration level of the hydraulic fluids in PCE. It was also observed that the ester peak splits into two major spectral peak areas ( $\sim 1753\sim 1724$ )  $\text{cm}^{-1}$  and ( $\sim 1724\sim 1708$ )  $\text{cm}^{-1}$  which may probably be due to inter- and intra-molecular interactions of solvent molecules with the analyte. Ester peak (absorbance) areas ( $\sim 1753\sim 1724$ )  $\text{cm}^{-1}$ , ( $\sim 1724\sim 1708$ )  $\text{cm}^{-1}$  and the sum of the areas [ $(\sim 1753\sim 1724)+(\sim 1724\sim 1708)$ ]  $\text{cm}^{-1}$  were evaluated for the development of calibration curves. Average of the three net absorbance (area) values obtained for a particular spectral region was used for the preparation of the calibration curve. Regression analysis was done for each calibration curve using analyte concentration as an independent variable and absorbance area as a dependent variable. The validation of the model is presented in the form of correlation coefficient  $R^2$ .

Data resulting from the utilization of spectral peak areas ( $\sim 1753\sim 1708$ )  $\text{cm}^{-1}$  and ( $\sim 1753\sim 1724$ )  $\text{cm}^{-1}$  for Tapmatic Cutting Fluid and MIL-H-83282 was found to be very erratic. Hence efforts focused on

the use of spectral peak areas ( $\sim 1724\sim 1708$ )  $\text{cm}^{-1}$  and the sum of  $[(\sim 1753\sim 1724)+(\sim 1724\sim 1708)]$   $\text{cm}^{-1}$  for the development of calibration curves; the purpose was to observe which of the areas result in higher  $R^2$ . Calibration curves developed at different time intervals within a 9-month period for ( $\sim 1724\sim 1708$ )  $\text{cm}^{-1}$  and  $[(\sim 1753\sim 1724)+(\sim 1724\sim 1708)]$   $\text{cm}^{-1}$  ester spectral peak areas gave  $R^2$  values of 0.87-0.99 for 1-20 mg/L concentration range while it was 0.972-0.998 for 1-10 mg/L concentration range utilizing the same spectral data. High  $R^2$  values demonstrate that infrared is a highly viable method for detecting low mg/L levels of hydraulic fluids in PCE. Variation in slopes of the calibration curves reflected that it is necessary to develop a new calibration curve whenever unknown samples are going to be analyzed for low analyte detection work.

Analytical work was carried out to check the performance (stability) of the instrument for obtaining data on different days. Pooled percent coefficient of variation (pooled % CV) for ( $\sim 1724\sim 1708$ )  $\text{cm}^{-1}$  spectral peak area for the mixture of hydraulic fluids was found to be 5.82% which was comparable to 8.6% and 3.16% obtained for individual MIL-H-83282 fluid and Tapmatic cutting fluid respectively. Pooled % CV for the  $[(\sim 1753\sim 1724)+(\sim 1724\sim 1708)]$   $\text{cm}^{-1}$  spectral peak area for hydraulic fluids mixture standards was found to be 2.78% as compared to 6.82% and 6.35% for individual MIL-H-83282 fluid and Tapmatic cutting fluid respectively. Low values<sup>7</sup> obtained for pooled % CV reflect that the instrument is stable for daily routine work to detect low levels of hydraulic fluids in PCE.  $R^2$  value of 0.98 and pooled % CV of 2.78% calculated for  $[(\sim 1753\sim 1724)+(\sim 1724\sim 1708)]$   $\text{cm}^{-1}$  spectral peak area were found to be superior as compared to  $R^2$  of 0.95 and pooled % CV of 5.82% for ( $\sim 1724\sim 1708$ )  $\text{cm}^{-1}$  spectral peak area. It demonstrates that it is appropriate to utilize the spectral area under  $[(\sim 1753\sim 1724)+(\sim 1724\sim 1708)]$   $\text{cm}^{-1}$  for the development of calibration curve for the purpose of calculating PCE extractable hydraulic fluids residue on small aerospace hardware (field samples) as NVR material.

#### **Field Work Done at the Kennedy Space Center**

Combination of small SS aerospace hardware parts (recycled / or certified cleaned / or tainted) and which could fit directly in 2 oz. amber colored bottles were used for the determination of NVR material by infrared and gravimetric methods. The total calculated exposed surface area of the samples for PCE extraction of hydraulic fluids residue ranged from 0.052164  $\text{ft}^2$  - 0.208333  $\text{ft}^2$ . NVR material was not detected in one set of samples. This may be that the parts used for PCE extraction work were reasonably clean or perhaps not enough parts were used for extracting a significant amount of NVR with PCE which could be detectable by infrared method. The test was repeated with recycled identical  $\frac{1}{4}$ " SS caps (not certified cleaned). Average of the PCE extractable NVR material for this set of samples was found to 0.79  $\pm$  0.2 mg/ $\text{ft}^2$ . The results suggest that infrared method is probably reliable within a factor of two for low PCE extractable analyte detection work.

PCE extractable hydraulic fluids as NVR material for two tainted field samples (combination of different small parts per sample) by infrared method was found be 6.61 mg/ $\text{ft}^2$  and 0.27 mg/ $\text{ft}^2$ . The results reflect that we can detect low mg/ $\text{ft}^2$  of the NVR material in PCE extract for meeting the strict KSC specifications of  $\sim 2$  mg/ $\text{ft}^2$  for the NVR material in precision cleaning verification.

Spiking for analyte percent recovery was also carried out on field samples. Average percent recovery for the spiked PCE solutions containing 1.99 mg/L and 5.26 mg/L of the mixture of three hydraulic by the infrared method was found to be 134% and 55% respectively. The results, again, reflect that the reliability of the analytical determination by infrared method is probably of the order of two for low ( $\sim 1\text{-}5$ ) mg/L analyte detection work.

Gravimetric method is extremely sensitive to errors when one is dealing with small amounts of NVR material. In our work,  $<1$  mg of the NVR was obtained for most of the field samples analyzed by gravimetric method, and normally, the precision of an analytical balance in this range is extremely poor. It reflects that gravimetric methodology is not appropriate for the detection of small amounts ( $\sim 1\text{-}5$  mg/ $\text{ft}^2$ ) of PCE extractable NVR material for clean validation of small aerospace hardware.

#### **CONCLUSIONS**

Results obtained on the quantification of industrial hydraulic fluids in perchloroethylene (PCE) has demonstrated that it is possible to detect 1-20 mg/L concentration levels of the analyte by infrared

method using appropriate ester absorption spectral peak area of the analyte. Correlation coefficients ( $R^2$ ) for calibration curves developed at various time intervals for mixtures of Yellow Tapmatic Cutting Fluid, Red Mil-H-5606 fluid and Red Mil-H-83282 fluid in PCE utilizing  $[(\sim 1753\sim 1724)+(\sim 1724\sim 1708)]\text{ cm}^{-1}$  and  $(\sim 1724\sim 1708)\text{ cm}^{-1}$  ester spectral peak areas were found to be between 0.87-0.99 for 1-20 mg/L range, and 0.842-0.998 for 1-10 mg/L range.

Results have demonstrated that it is possible to detect  $\sim 1\text{ mg/L}$  of industrial hydraulic fluids in PCE under the experimental conditions of the test runs utilizing sum of the areas  $[(\sim 1753\sim 1724)+(\sim 1724\sim 1708)]\text{ cm}^{-1}$  in the ester spectral peak region. Pooled percent coefficients of variation for sets of individual as well as mixture of hydraulic fluids standard dilutions were found to be in the range of 2.78-8.6% demonstrating a stable instrumental performance for detecting low mg/L concentration levels of industrial hydraulic fluids in PCE.

Data obtained on the non-volatile residue material extractable with PCE from small aerospace hardware has demonstrated the viability of utilizing infrared method for precision cleaning verification. It has demonstrated that we can detect  $\sim 1\text{-}5\text{ mg/ft}^2$  of PCE extractable industrial hydraulic fluids residue as NVR material with a reliable factor of two.

### RECOMMENDATIONS

In this study, a few field samples were analyzed for the determination of PCE extractable NVR material by the infrared method. High  $R^2$  values obtained for the developed calibration have reflected that it is possible to use PCE for the determination of hydraulic fluids residue on the small aerospace hardware as NVR material, however, more data may be needed before making a critical evaluation on the routine applicability of the developed infrared methodology. It is recommended that a 6-12 month study should be carried out on the applicability of the developed methodology using real world samples.

Another suggestion is the participation in laboratory testing programs (as that of Environmental Protection Agency or Water Program of the Department of Interior) to evaluate the applicability of the infrared method for the detection of NVR material extractable with PCE.

The methodology developed utilizing PCE as an extraction solvent for hydraulic fluids residue may be extended as a replacement for Freon-113 procedure. It may replace any procedure, based on solvent extraction and subsequent quantification by infrared or gravimetric (only high mg/L level) method. However, its applicability to water samples will require laboratory and field studies. Efforts made in this project concentrated on the extraction of the ester-based hydraulic fluids residues with PCE. No efforts were made to address the effectiveness of PCE as an extracting solvent with respect to Freon-113 which is a standard methodology at KSC for clean validation of small aerospace hardware.

### REFERENCES

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